

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
10 May 2001 (10.05.2001)

PCT

(10) International Publication Number  
**WO 01/32809 A1**

- (51) International Patent Classification<sup>7</sup>: C10L 1/02, C10G 27/12, 67/12, C10L 1/18, 10/02
- (21) International Application Number: PCT/EP00/10829
- (22) International Filing Date: 31 October 2000 (31.10.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
9925971.5 3 November 1999 (03.11.1999) GB
- (71) Applicant (for all designated States except US): EXXON CHEMICAL PATENTS INC [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): CAERS, Raphael, Frans, Ivo [BE/BE]; Prins Boudewijnlaan 189, B-2620 Belgium (BE). CHU, John, W. [US/US]; 484 Whiton Road, Neshanic Station, NJ 08853 (US). DAKKA, Jihad, Mohammed [IL/BE]; Heikneuterlaan 7, B-3010 Kessel-Lo (BE). YEH, Lisa, I. [US/US]; 14 Denver Road, Marlton, NJ 08053 (US).
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
- With international search report.
  - Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: REDUCED PARTICULATE FORMING DISTILLATE FUELS

(57) Abstract: Distillate fuel is selectively oxidised, preferably by hydrogen peroxide in the presence of a titanium silicalite catalyst to produce hydroxyl and/or carbonyl groups bonded to paraffinic carbon atoms of the diesel fuel molecules to provide at least 0.1 wt %, preferably at least 0.3 wt %, oxygen in the fuel. The fuel, which yields lower particulate emissions on combustion preferably, has a low sulphur, polycyclic aromatics and olefin content and a high cetane number.

WO 01/32809 A1

**REDUCED PARTICULATE FORMING DISTILLATE FUELS**

The present invention relates to fuels, which are atomised for combustion such as distillates,  
5 particularly diesel fuels having improved environmental performance upon combustion.

Whilst diesel fuels have many advantages they suffer from the disadvantage that they  
produce undesirable polluting emissions on combustion. These are particularly problematic  
with diesel engines where the emissions are discharged into the atmosphere in the exhaust  
gases of diesel powered vehicles. Similar, albeit less severe problems arise from the  
10 combustion of heating oils. The invention is also applicable to stationary and marine motors  
which operate through fuel injection of heavier distillate fuels.

Middle distillates and the heavier marine fuels are typically obtained by distillation, cracking  
and fractionation of crude oil. They are complex mixtures and the pollutants generated by  
15 their combustion take several forms. The presence of sulphur in the fuel results in sulphur  
containing pollutants, particularly oxides of sulphur and sulphates. The presence of nitrogen  
in the fuel and in the air in which the fuel is combusted leads to the formation of oxides of  
nitrogen (otherwise known as NOX). The presence of polynuclear aromatics in the fuel can  
lead to PNA emissions. Furthermore, the combustion process involving ignition of atomised  
20 fuel particles as opposed to vaporised fuel (as in gasoline powered engines) can lead to  
incomplete combustion of the fuel in the engine or the burner which can result in the  
formation of particulates or soot particles in the exhaust gases.

These are not new problems and for many years refiners have been developing their  
25 refining technology to produce middle distillate fuels and heavy fuels which lead to reduced  
emissions. Engine and burner manufacturers have developed improved equipment to

reduce emissions and additive suppliers have developed additives to enhance combustion and enable the use of fuels that are more environmentally friendly.

There is however a continuing need which is reflected in the legislation to provide fuel compositions that generate lower and lower levels of pollutants on combustion. This is  
5 illustrated by the specifications set in Europe for diesel fuels in which the maximum level of sulphur permissible in 1995 was 500 ppm, in the year 2000 it will be 350 and it is anticipated that in the year 2005 it will be 50 ppm and the European Union directive concerning the emission of gaseous and particulate pollutants from diesel engines. These specifications  
10 and trends are set out in the Oil & Gas Journal (OGJ) Special on "Future Transport Fuels" 12 July 1999 the article Page 40 to 45 by Nigel R. Cuthbert titled "Auto and Oil Industries Improving Quality, Efficiency of EU Fuels", particularly the Table 2 on Page 44. The "Official Journal of the European Communities" L350/58-L350-68 "Directive 98/70/EC of the European Parliament and the Council of 13 October 1998 relating to the quality of petrol and  
15 diesel fuels and amending Council Directive 93/12/EEC", of which Annex II (Page L350/66 contains the specifications for diesel for the year 2000 (350 mg/kg max sulphur content), and Annex IV Page L350/68 contains those for the year 2005. Similarly the amount of polycyclic aromatics permitted is being reduced as is the proportion of high boiling materials and, at the same time the cetane number which is a measure of the combustion ability of  
20 the fuel is being increased.

Accordingly, there remains a need for technology, which provides distillate fuels, which are cleaner burning and satisfy the imminent more stringent environmental requirements.

The present invention is concerned with distillate fuels and their production, particularly fuels boiling in the middle distillate region, which have improved combustion and in particular fuels which generate lower particulate emissions on combustion.

5 It has long been recognised that soot particles are formed in diesel fuel due to incomplete combustion often caused by incomplete mixing of the fuel and the combustion air before actual combustion. Various attempts have been made to enhance combustion for example, it has been proposed in WO 97/42405 to inject a fluid containing a peroxide into the combustion chamber, preferably after the initiation of the combustion phase. U.S. Patent  
10 4 723 963 oxidises the benzylic carbon atoms in aromatics in the fuel by free radical oxidation to increase the cetane number of the fuel. It is notable that the aromatic levels required in the fuels of U.S. Patent 4 723 963 are higher than those of modern day fuels. Furthermore, U.S. Patent 4 723 963 clearly states that paraffinic hydrocarbon moities should not be oxidised since it is these hydrocarbyl groups, which provide a desirable high cetane  
15 number. As early as the 1940's U.S. Patents 2 317 968 and 2 365 220 suggested oxidation of diesel fuel by free radical oxidation.

It is also well known to incorporate additives, which improve the cetane number of the fuel. United States Patents 5 114 433 and 5 114 434 are concerned with improving the cetane  
20 numbers of directly distilled fuel and visco-reduced diesel fuels respectively. These patents are aimed at overcoming the disadvantage with cetane improver additives and the selection of the additive is restricted to one that is simultaneously relatively insoluble in water and chemically stable relative thereto, sufficiently soluble in diesel fuel, stable, non-corrosive and non-toxic. In these patents the cetane number of the fuel is increased by contacting the  
25 diesel fuel with either hydrogen peroxide in the presence of formic acid, acetic acid or propionic acid or with performic acid, per-acetic acid or perpropionic acid optionally in the

presence of hydrogen peroxide. These patents do not indicate the nature of the product produced by contacting the fuel with the radical, peroxide based materials and attempts to repeat the processes have not resulted in any oxidation of the fuel. It is however believed that if any reaction takes place a complex mixture will be formed containing peroxide, ester, and acid groups. These groups would have a deleterious effect on the short and long term stability of the fuel and any acid functions may render the fuel corrosive.

United States Patent 5 324 335 discloses synthetic diesel fuel produced by the Fischer Tropsch Synthesis. This produces a fuel containing primary alcohols to give a 3 % wt oxygen content and it is speculated that the presence of the alcohols contributes to superior performance in relation to particulate airborne emissions.

The present invention is concerned with the reduction in particulates formed from the combustion of fuels and is applicable to fuels containing a broad range of sulphur level typically from over 500 ppm to less than 30 ppm. In particular we have found that distillate fuels, particularly middle distillates containing less than 350 ppm of sulphur may be oxidised to provide hydroxyl and/or carbonyl groups chemically bound to paraffinic molecules in the fuel and that the amount of particulates generated upon combustion of the oxidised fuel is significantly reduced when compared with the amount of particulates generated upon combustion of the unoxidised fuel. The invention may be used to reduce particulates from both high and ultra low (less than 50 ppm, particularly less than 30 ppm) sulphur fuels. We have also found that the techniques of the present invention may be used to reduce the sulphur and nitrogen levels of fuels, particularly to reduce the sulphur levels of fuels whose sulphur level is already relatively low.

In one aspect the present invention therefore provides a distillate fuel containing hydroxyl and/or carbonyl groups chemically bound to paraffinic carbon atoms within the distillate fuel molecules in an amount to provide at least 0.1 wt %, preferably at least 0.3 wt %, oxygen in the fuel.

5

The distillate fuel is preferably a middle distillate fuel such as petroleum distillate boiling in the range 150 to 550°C, preferably 150 to 450°C, more preferably 150 to 400°C and may be obtained by atmospheric or vacuum distillation of crude oil which may have been subjected to cracking. The fuels of the present invention are particularly useful as diesel fuels. It is particularly preferred that the distillate have a 95 vol % distillation point (as determined by EN-ISO 3405 (1988)) no greater than 370°C, preferably no greater than 360°C. The fuel preferably has a density no greater than 845 Kg/m<sup>3</sup> and a sulphur content below 350 ppm preferably below 50 ppm which is generally achieved by hydrodesulphurisation.

10

15

Whilst the invention is applicable to a range of fuels it is particularly useful in the production of fuels satisfying the emerging stricter environmental specifications. Here it is further preferred that the fuel from which the fuels of the present invention are derived contain no more than 11 wt % polycyclic aromatics, no more than 15 wt % olefins and have a cetane number of at least 50, preferably at least 52. The invention is however also concerned with the heavier distillate fuels used for stationary and marine motors such as the fuels sometimes known as bunker fuels and the heavier poorer quality fuels sometimes used in diesel vehicles. Where the fuel has a high olefine content, care must be taken to avoid any cleavage of the molecules in the fuel during the oxidation reaction, which can form undesirable acid functions. We therefore prefer that the olefin content of the fuel that is to be oxidised is below 10%, more preferably below 5%. A bromine number below 1.5, preferably 0.5 or less is most preferred.

20

25

We prefer that the oxidised fuel contains from 0.3 to 15 wt %, more preferably 0.5 to 15 wt % oxygen particularly 1 to 10 wt %. An oxygen content of 1 to 4 wt % is preferred and 2 to 3 wt % is most preferred.

5

The term paraffinic carbon atom means a saturated carbon atom, which is attached to at least one hydrogen atom and not attached directly to an aromatic nucleus. Paraffinic carbon atoms may be of the formula  $CR_nH_m$  where R is an alkyl or alkylidene group  $m + n$  is 4 and m is 1 or 2. The distillate fuel molecules are those that are separated in the refinery during the distillation process used in the production of the fuel and the hydroxyl or carbonyl groups are provided by oxidation of these molecules, the hydroxyl groups are generally secondary or tertiary hydroxyl groups.

The hydroxyl and/or carbonyl groups in the fuel are conveniently provided by selective oxidation of the fuel. Processes suitable for the oxidation of the fuel are described in European Patent 0376453 B, PCT Applications WO 93/04775, WO 90/05126 and WO 93/15035, United States Patents 5 021 607 and 5 739 076 and UK Patent Application 9406434.2.

These patent documents describe various titanium containing silicon-based zeolites, which have been found to be particularly useful catalysts for the oxidation of saturated paraffinic carbon atoms with peroxides such as hydrogen peroxide to yield hydroxyl or carbonyl groups. The processes of these patent documents result in selective oxidation to hydroxyl and carbonyl groups unlike the free radical processes of the prior art. Use of these processes enables fuel to be obtained in which 70% and preferably 80% or more of the oxygen bound to the paraffinic carbon atoms in the fuel is in the form of hydroxyl and/or

carbonyl groups giving a significant improvement in fuel performance. The hydroxyl groups produced by these processes are predominantly secondary and tertiary hydroxyl groups and all the hydroxyl groups may be secondary and/or tertiary. Where carbonyl groups are formed it may be desirable to selectively hydrogenate them to hydroxyl groups by for  
5 example standard hydrogenation techniques using heterogeneous catalysts.

The present invention therefore further provides a process comprising selectively oxidising paraffinic carbon atoms in distillate fuel molecules in a distillate fuel boiling in the range 150°C to 400°C to provide fuel containing hydroxyl and/or carbonyl groups bonded to  
10 paraffinic carbon atoms and an oxygen content of at least 0.1 wt %, preferably at least 0.3 wt %.

In a preferred embodiment of the process, the fuel is selectively oxidised with organic peroxides, ozone or hydrogen peroxide in the presence of a titanium zeolite catalyst having  
15 an infrared absorption band around 950 cm<sup>-1</sup> or 960 cm<sup>-1</sup>. Hydrogen peroxide is particularly preferred as the oxidising agent. The catalyst is preferably in powder, pellet, tablet or granular form and may be mixed with inert materials such as support or binding materials. The catalyst may also be mixed with other materials such as zeolites.

20 The preferred catalysts are based on crystalline synthetic material comprising silicon, alumina and titanium oxides as discussed in J Chem Soc Chem Commun 1992, Page 589 and "The Preparation, Characterization and Catalytic Properties of Titanium Containing Zeolites" by A. J. H. P. Van de Pol – PhD Thesis at Eindhoven University (NL) 1993 and are characterised by an infra red absorption band at around 950 cm<sup>-1</sup> or 960 cm<sup>-1</sup>. The catalysts  
25 should have free or accessible titanium in their structure and are typically of the general formula:



$\text{SiO}_2:\text{TiO}_2:\text{Al}_2\text{O}_3$  at varying ratios although  $\text{Al}_2\text{O}_3$  is not an essential component.

These catalysts may be prepared from a mixture containing a source of silicon oxide, a source of titanium oxide, optionally a source of aluminium oxide, a nitrogenated organic base and water as described in J Chem Soc Chem Commun 1992, Page 589, in United States Patent 5 021 607 or in Patent Application WO 97/33830 or by the dealumination of ZSM-5 and reaction with titanium tetrachloride vapour as described by B. Kraushaar and J. H. C. Van Hoof in Catalysis Letters 1 (1988) Pages 81-84. The catalysts may contain small amounts of other metals such as aluminium, gallium and iron (as described in European Patent Application 0226258). The catalyst may also be a dual catalyst which enables the production of hydrogen peroxide in situ from oxygen and hydrogen on a noble metal such as Palladium (as described in WO 00/135894). The dual catalyst may be prepared by impregnating the titanium containing zeolite with the noble metal.

United States Patent 4 824 976 relates to the use of these types of catalysts for the epoxidation of olefins with  $\text{H}_2\text{O}_2$  and in this patent x may be in the range from about 0.0001 to about 0.04. United Kingdom Patents 2083816 and 2116974 relate to the use of similar catalysts for the introduction of hydroxy groups into aromatic substrates by oxidation with  $\text{H}_2\text{O}_2$ . These patents are incorporated herein by reference for their descriptions of the infrared and x ray diffraction analyses of the catalysts; as stated the band intensity at approximately  $950\text{ cm}^{-1}$  increases as the quantity of titanium present increases.

We prefer to use the titanium beta form since it has a pore size that can readily accommodate the distillate molecules (typically  $\text{C}_{14}\text{-C}_{17}$  hydrocarbons) to be oxidised and can cause a greater conversion in the oxidation reaction.

The catalysts may be prepared by:

- i) heating a reaction mixture comprising:
  - 5 a) a silicon oxide source ( $\text{SiO}_2$ )
  - b) a titanium oxide source ( $\text{TiO}_2$ )
  - c) optionally an aluminium oxide source
  - d) optionally an alkali metal source
  - e) a nitrogen containing organic base, and
  - 10 f) water
- ii) separating the formed crystals from the reaction mixture, and
- iii) calcining the separated crystals to form the catalyst.

The catalyst used in this invention is preferably prepared from a reaction mixture consisting  
15 of sources of silicon oxide, titanium oxide, aluminium oxide and possibly an alkaline oxide, a nitrogen containing organic base and water, the composition in terms of the molar reagent ratios being as heretofore defined.

The silicon oxide source can be a tetraalkylorthosilicate, preferably tetraethylorthosilicate, or  
20 simply a silicate in colloidal form.

The titanium oxide source is a hydrolysable titanium compound preferably chosen from  $\text{TiCl}_4$ ,  $\text{TiOCl}_2$  and  $\text{Ti}(\text{alkoxy})_4$ , preferably  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ . When used, the aluminium oxide source can be aluminium salts or aluminium metal.

25

The organic base is tetraalkylammonium hydroxide, and in particular tetramethylammonium hydroxide.

In the preferred method to produce the catalyst the mixture of these reactants is subjected to hydrothermal treatment in an autoclave at a temperature of between 130 and 200°C under its own developed pressure, for a time of 1 to 30 preferably 6 to 30 days until the crystals of the catalyst precursor are formed. These are separated from the mother solution, carefully washed with water and dried. When in the anhydrous state they have the following composition:



The mixture is preferably heated in an autoclave at a temperature of 130 - 200°C, preferably about 175°C, for about 10 days to cause crystallisation.

The precursor crystals are then heated for between 1 and 72 hours in air at 550°C to eliminate the nitrogenated organic base.

The final catalyst has the following composition:  $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{TiO}_2$

The preferred molar ratio (MR) of the different reactants with regard to the silicon oxide source ( $\text{SiO}_2$ ) are mentioned in the following table:

	MR	MR (preferred)
$\text{SiO}_2/\text{Al}_2\text{O}_3$	0-Infinite	70-1000
$\text{OH}/\text{SiO}_2$	0.1-0.8	0.2-0.4
$\text{TiO}_2/\text{SiO}_2$	0.005-0.5	0.01-0.04
$\text{H}_2\text{O}/\text{SiO}_2$	20-200	5-15
$\text{RN}^+/\text{SiO}_2$	0.1-1.0	0.3-0.9

The catalyst may be agglomerated in powder, pellet or tablet form, to form crystal clusters, which are also active and readily recovered after the oxidation reaction. The catalyst may also include a carrier and/or a support. The preferred catalysts are the Titanium Silicalite catalyst known as TS-1 and the Alumino Titanium Silicalite known as Titanium-Beta.

The oxidising agent used to oxidise the distillate fuel may be hydrogen peroxide or an organic peroxide; hydrogen peroxide is preferred and may be added as such or prepared in situ as previously described. It is also preferred that the diesel fuel is liquid or in the dense phase at the conditions used for the oxidation reaction. It is also preferred that if hydrogen peroxide is used the hydrogen peroxide is used as an aqueous solution and the reaction is carried out in the presence of a solvent. Where an organic peroxide is used, a solvent may not be required or the peroxide itself may act as the solvent.

By the present invention employing selective catalytic oxidation it is possible to oxidise saturated aliphatic or cyclic compounds in the distillate fuel, including aliphatic substituents of alkyl aromatic compounds to produce secondary and/or tertiary hydroxyl and/or carbonyl groups. The saturated groups which may be oxidised by the process of this invention include long or short, branched or linear alkanes containing 3 to 22, typically 3 to 18, more preferably 12 to 18 carbon atoms, cyclic alkanes and mono- and poly- alkyl aromatics in which at least one of the alkyl groups contain at least three, more preferably 3 to 18, most preferably 12 to 18 carbon atoms and mono- and poly- alkyl cyclic alkanes.

We have surprisingly found that by the selection of appropriate conditions the saturated groups in the distillate fuel may be oxidised with high selectivity to alcohols and carbonyls under relatively mild conditions. The reaction conditions, choice of catalyst, quantities of

catalyst used and the proportions of oxidising agent to distillate fuel will depend upon the composition of the distillate fuel and the desired oxygen level.

The aliphatic substituent may be a part of a totally aliphatic compound, an aryl compound  
5 (alkylaromatic) or an alkylnaphthene compound. Furthermore, said compound may contain other functional groups which have electron-repulsive properties and which, accordingly, are not reactive. The catalytic oxidation may also oxidise residual sulphur compounds in the fuel. This can convert the sulphur species to ones more readily removable and thus the present invention can bring the additional benefit of enabling a further reduction in sulphur  
10 levels.

We have found that the reactivity sequence for the aliphatic compounds slows down from tertiary to secondary to primary carbon atoms.

15 The oxidising agents used in the reaction may be organic peroxides, ozone or hydrogen peroxide either added or prepared in situ, aqueous hydrogen peroxide being preferred. The aqueous solution contains from 10 to 100, preferably 10 to 70 wt % hydrogen peroxide for example diluted hydrogen peroxide (40% by weight in water). It is also preferred that a polar solvent be present for example a ketone or an alcohol, acetone, methanol, ethanol or  
20 butanol being preferred. The solvent will increase the solubility of the distillate fuel in the H<sub>2</sub>O<sub>2</sub> aqueous phase when aqueous hydrogen peroxide is used.

Particular advantages of the process of the present invention are that it uses mild temperature and pressure conditions and the conversion and yield are high and by-product  
25 formation is small. In particular the conversion of hydrogen peroxide is high. We do however prefer that the conversion of the hydrocarbon is relatively low and less than 30%.

Above 30% conversion there is a risk that di-ketones will be formed leading to cleavage of the oxidised molecules and perhaps the formation of acid functions in the oxidised fuel. The presence of these acid functions can lead to the fuel being corrosive. We therefore prefer to use less than a stoichiometric amount of hydrogen peroxide based on the distillate fuel. It is also preferred that the oxidised fuel have a Total Acid Number below 1 mgKOH/gm, preferably 0.5 mgKOH/gm, more preferably below 0.2 mgKOH/gm. If the fuel is over oxidised to a TAN above these levels it may be necessary to remove acids by, for instance, caustic washing.

- 10 The optimum reaction temperature for oxidation is between 50 and 150°C, preferably about 100°C. The pressure should be such that all materials are in the liquid or dense phase.

The reaction can be carried out at room temperature but higher reaction rates may be obtained at higher temperatures, for example under reflux conditions. Reflux conditions may be used or the autogeneous pressure created by the heated reactants whereby use of a pressurised reactor enables still higher temperatures to be reached. Use of higher pressures in the range of 1 to 100 bars ( $10^5$  to  $10^7$  Pa) can increase the conversion and selectivity of the reaction. The oxidation reaction can be carried out under batch conditions or in a fixed bed, and the use of the heterogeneous catalyst enables a continuous reaction in a monophasic or biphasic system. The catalyst is stable under the reaction conditions, and can be recovered and reused.

The process of the present invention is preferably carried out using hydrogen peroxide in the presence of a solvent. The solvent is important as it enables the distillate fuel and the hydrogen peroxide to interact and come in contact with the catalyst. It should therefore

either dissolve in the diesel fuel and the aqueous phase, which is generally present due to the use of aqueous hydrogen peroxide as the oxidising agent, or enable the two phases to diffuse into each other. Polar compounds are preferred and examples of preferred solvents are supercritical carbon dioxide, alcohols, ketones, ethers, glycols and acids with a number of carbon atoms which is not too high, preferably less than or equal to 8. Methanol or tertiary butanol are the most preferred of the alcohols, acetone the most preferred of the ketones, and acetic or propionic acid the most preferred acids. Mixtures of these solvents may also be used. The amount of solvent is important and can influence the reaction product and the conversion, the choice of solvent and the amount depending on the composition of the distillate fuel. The solvent improves the miscibility of the hydrocarbon phase and the aqueous phase, which is generally present due to the use of aqueous hydrogen peroxide as the oxidising agent.

The techniques of the present invention provide the additional benefits that the oxidation reaction can convert sulphur species in the distillate fuels to more polar species that are more easily removed. For example, distillate fuels contain sulphur in the form of thiophenes, sulphides and mercaptans and these can be converted to sulfoxides and sulphones by the oxidation techniques employed in the present invention. These more polar sulfoxides and sulphones can then be removed by distillation, washing with water or polar solvents or absorption on for instance silica gel. This is particularly useful in the further reduction of the sulphur levels of fuels that have already been subjected to hydrodesulphurisation to reduce their sulphur levels to below 200 ppm particularly below 100 ppm and more particularly below 50 ppm. Although the techniques would be operable at higher sulphur levels the large quantities of hydrogen peroxide required could render the techniques unattractive.

The techniques of this invention are also useful in the reduction of the nitrogen level in the fuel as the oxidation reaction will convert nitrogen containing species to nitrogen oxides which can be readily removed by distillation, washing with water or polar solvents or absorption on for instance silica gel, when used, the removal of the nitrogen species is preferably the same operation as the removal of the oxidised sulphur species.

The presence of the hydroxyl and/or carbonyl groups of the fuel may be determined by standard NMR techniques such as those described in Spectroscopic methods in Organic Chemistry by D. H. Williams and I. Fleming published by McCraw Hill Publishing Company.

Infra Red Spectroscopy and Gas Chromatography including Gas Chromatographic Mass Spectrometry may also be used. The presence of hydroxyl groups is indicated by bands in the infra red spectrum at around 3500 and carbonyl groups by bands around 1710. These techniques can also be used to determine if the hydroxyl groups are primary, secondary or tertiary; secondary and tertiary groups being preferred.

The distillate fuel of the present invention may be treated with additives to improve its performance.

Whilst the oxidised fuels of the present invention show a significant reduction in particulate formation on combustion of the fuel, the impact on hydrocarbon and carbon monoxide emissions is less and may, in some instances, involve a slight increase. These can however be overcome by the use of a typical exhaust oxidation catalyst in the engine exhaust system.

Heating oils and other distillate petroleum fuels, such as diesel fuels, contain alkanes that at low temperatures tend to precipitate as large crystals of wax in such a way as to form a gel



structure, which causes the fuel to lose its ability to flow. The lowest temperature at which the fuel will still flow is known as the pour point. As the temperature of the fuel falls and approaches the pour point, difficulties arise in transporting the fuel through lines and pumps. Further, the wax crystals tend to plug fuel lines, screens, and filters at temperatures above the pour point. These problems are well recognised in the art, and various additives have been proposed, many of which are in commercial use, for depressing the pour point of fuel oils. Similarly, other additives have been proposed and are in commercial use for reducing the size and changing the shape of the wax crystals that do form. Smaller size crystals are desirable since they are less likely to clog a filter; certain additives inhibit the wax from crystallising as platelets and cause it to adopt an acicular habit, the resulting needles being more likely to pass through a filter than are platelets. The additives may also have the effect of retaining in suspension in the fuel the crystals that have formed, the resulting reduced settling also assisting in prevention of blockages.

Effective wax crystal modification (as measured by the Cold Filter Plugging Point (CFPP) test and other operability tests, as well as simulated and field performance) may be achieved by the addition of ethylene-vinyl acetate or ethylene-vinyl propionate copolymer-based flow improvers.

In U.S. Patent 3 961 916 middle distillate flow improvers are described which comprise a wax growth arrestor and a nucleating agent, the former being preferably a lower molecular weight ethylene-vinyl ester copolymer with a higher ester content, the latter preferably a higher molecular weight copolymer with a lower ester content, the esters preferably, but not necessarily, both being vinyl acetate.

In DE-A-2407158 middle distillate flow improvers are described, comprising a mixture of low molecular weight ethylene-vinyl ester and ethylene-acrylic acid ester copolymers, both containing at least 40 mole per cent of the ester component.

- 5 FR-A-2061457 describes a mixture of copolymers comprising a first copolymer of ethylene and an olefinically-unsaturated monomer containing 3 to 30 carbon atoms and having an average molecular mass between 700 and 3000, and a second copolymer of ethylene and an olefinically-unsaturated monomer containing 3 to 60 carbon atoms and having an average molecular weight above 3000 and up to 60,000.

10

EP 0648257 describes a fuel oil additive effective to improve low temperature flow of the oil, and is based on the observation that a composition comprising at least two different copolymers of ethylene with an unsaturated ester, or a composition comprising a copolymer of ethylene with at least two different types of unsaturated ester-derivable units, is an effective cold flow improver having advantages over previously proposed compositions.

15

Examples of other additives, which may be included in the distillate fuels, are cetane improvers, antifoam additives, dispersants such as alkyl succinimides, dyes and antioxidants. More recently lubricity additives such as esters have been incorporated into diesel fuels to compensate for the reduction in lubricity caused by the deep hydrofining used to reduce the sulphur level in the fuel, the incorporation of oxygen into the fuel according to the present invention may however improve the lubricity of the fuel. Lubricity is required to prevent wear in the pumps in diesel engines.

20

- 25 We believe that the introduction of the hydroxyl and/or carbonyl groups will not cause any adverse interaction with other additives present in diesel fuel. The oxidised fuels of the

present invention may be used on their own as diesel fuels, or fuels for stationary or marine engines. Alternatively they may be blended with other distillate fuels and/or with biofuels such as the fuels derived from rapeseed methyl ester or soybean ester.

- 5 We believe that, unlike many other modified fuels, the fuels of the present invention will perform well in conventional engines such as diesel engines operating under standard conditions and without the need of special lubricants. The introduction of the hydroxyl and/or carbonyl groups in the fuel will not cause adverse interactions with the lubricant or the lubricant additives that it encounters at the fuel lubricant boundary. We further believe  
10 that, depending upon the composition of the diesel, particulate formation during fuel combustion can be reduced by 5 to 50% and at times by more.

- Emissions testing may be carried out on a commercial vehicle with a direct-injection diesel engine (eg VW Golf 1.9 TDi). The vehicle, with engine warmed-up, may be driven over the  
15 legislated European drive cycle for emissions measurement. This consists of 4 "elementary urban cycles" (ECE-15) and one 'extra-urban cycle' (EUDC) and covers a range of speeds and loads.

- A particulate tunnel connected to the vehicle exhaust may be used for particulate collection.  
20 Particulates can be collected on pre-conditioned and weighed filter papers, one for the ECE phase and one for the EUDC phase of the drive cycle. The filter papers can then be re-weighed after the test to determine the mass of particulates collected. Each test fuel is preferably tested 3 times over the ECE/EUDC cycle, and the base fuel tested before and after the 3 test fuel repeats.

25

On an industrial scale, distillate fuel of this invention may readily be produced by the oxidation of a suitable refinery stream such as a stream boiling in the range of 230 to 320°C. Alternatively a side stream may be oxidised and then blended with a normal distillate to produce a final fuel having the desired oxygen level, however, it may be difficult to produce a side stream with a sufficiently high oxygen level to produce the desired final level on blending without causing cleavage and acid formation. The oxidising unit in the refinery is preferably located downstream of the hydrofining unit currently used in most refineries to reduce the sulphur level of the fuel. This will increase the conversion to hydroxyl groups since the quantity of sulphur species; olefins and benzylic carbon atoms, which would otherwise react with the oxidising agent, have been reduced in the hydrofining operation. An additional unit may be provided downstream of the oxidising unit for the removal of oxidised sulphur and nitrogen species.

The present invention is illustrated by reference to the following Examples in which a distillate fuel was oxidised with hydrogen peroxide using either Titanium beta (Ti-β) or Titanium silicalite (TS-1) as the catalyst. The preparation of the TS-1 catalyst is described in European Patent 0376453 A.

#### EXAMPLE 1

The distillate fuel used had the following properties:

Distillation (°C) ASTM D	D86
IBP	162
5%	238
10	254
20	267
30	274
40	281
50	287
60	292
70	298
80	306
90	315
95	322
FBP	326
Aniline Pt N (°C)	66.2
Colour - D1500	1
Density (g/ml)at 15 °C	0.8502
Kin Visco (cSt)at 25 °C	4.83
Kin Visco (cSt)at 40 °C	3.38
Flash PT (°C) PM	68

Bromine Number: 1.20 g Br per 100 g of sample

The Aromatics content was: 32.9% wt by PINA (ASTM D2786)

- 5 The Sulphur content was 0.52 wt %

Carbon number distribution (wt %) by capillary gas chromatography

C5	0.1 wt %
C6	0.1 wt %
C7	0.3 wt %
C8	0.5 wt %
C9	0.7 wt %
C10	1.1 wt %
C11	4 wt %
C12	2.1 wt %
C13	3.5 wt %
C14	6.0 wt %
C15	12.2 wt %
C16	15.4 wt %
C17	15.1 wt %
C18	15.2 wt %
C19	11.8 wt %
C20	9.0 wt %
C21	4.4 wt %
C22	1.1 wt %
C23	0.1 wt %

Since the fuel had relatively high sulphur levels and bromine numbers the consumption of hydrogen peroxide was high.

5

The Titanium Beta catalyst used was prepared as follows:

#### A SYNTHESIS

##### *Reactants*

Quantity grams	Name	Chemical formula	Abbreviation	Source
5.36	Tetra propyl ortho titanate	$(C_3H_7O)_4Ti$	TPOT	Jansen Chimica, 98%
0.63	Aluminium nitrate monohydrate	$Al(NO_3)_3 \cdot H_2O$	Al-nitrate	Aldrich, 99.99%
201.74	Tetra ethyl ammonium hydroxide	$(C_2H_5)_4NOH$	TEAOH	40% aqueous solution - Johnson Alfa
85 ml	demineralised water	$H_2O$	water	-
60	Aerosil 200	$SiO_2$	Aerosil	Degussa
0.216	seed			

*Gel composition (molar ratios)*

Si : Al : Ti : OH<sup>-</sup> : H<sub>2</sub>O = 1 : 0.003 : 0.018 : 0.55 : 15.7

The synthesis was started by placing 201.74 grams of TEAOH in a plastic container where it  
5 was stirred under nitrogen flow with a magnetic stirrer for 10 minutes. After stirring 100 ml  
of water was added. TPOT was then added drop wise while continuing to stir. 2.9 grams  
were added over 7 minutes; 1.8 grams were added over the following 5 minutes and the  
following 0.66 grams were added over 3 minutes. The total time for adding the total weight  
(5.36 grams) of TPOT was 15 minutes. 60 grams of Aerosil was then added: 10 grams,  
10 each quarter of an hour, until 50 grams of Aerosil had been added. At this point a solution  
of Al(NO<sub>3</sub>)<sub>3</sub> H<sub>2</sub>O (0.63 grams in 61.1 ml water) was added. Finally, the last portion of 10  
grams of Aerosil was added. The mixture was stirred for two hours under nitrogen flow.  
This resulted in a transparent and slightly thickened gel, which was heated up in a Teflon  
linear PARR autoclave (1 litre) to 135°C in 2 hours. The autoclave was then kept at 135°C  
15 for 240 hours.

*Washing and centrifuging and drying*

The solid phase was separated by centrifuging at 9000 RPM for 1 hour. The solid material  
was crushed and washed 4 times and subjected to a final centrifugation for 2 hours at  
20 11000 RPM. The material was then dried.

Finally the solid material was calcined under airflow. The calcination programme was as  
follows:

30°C → 550°C (60°C/hour)

25 550°C → 550°C (24 hours)

550°C → 120°C (60°C/hour)

**B**     CHARACTERISATION

5     The material was analysed by X-ray powder diffraction, scanning electron microscopy, Fourier transform infra red spectroscopy, (UV-VIS spectroscopy). Element analysis used atomic absorption spectrometry and photometry (colorimetry).

**C**     OXIDATION

10     The oxidation reactions were performed at the temperature indicated in Table 1 using the Ti-β prepared as above and the TS-1 prepared according to EP 0376453 A. The process used is described in U.S. Patent 5 021 607 with ratios of hydrogen peroxide to distillate fuel set out in Table 1 below, the reactions were performed at reaction temperature for 6 hours whilst stirring at 520 rpm. The properties of the  
15     materials obtained are also set out in Table 1.

The oxygen contents are approximate and were calculated from the NMR data and assumed the composition of the starting distillate fuel to be C<sub>12</sub>H<sub>26</sub>.



Table 1:

Run No	Catalyst, g	Solvent (@ 70 volume %)	Reaction temperature °C	Ratio H <sub>2</sub> O <sub>2</sub> /Substrate	H <sub>2</sub> O <sub>2</sub> Efficiency, %O to ROH or carbonyl	Oxygen content wt %	RCOOH, %
1	Ti-β (0.6)	Acetone	130	1/3	36	1.02	ND
2	TS-1 (0.6)	Acetone	130	1/3	8	0.23	ND
3	TS-1 (0.6)	TBA	130	1/3	5	0.14	ND
4	TS-1 (1.8)	TBA	130	4/1	30	2.6	~11
5	Ti-β (1.8)	TBA	130	4/1	54	4.6	~5
6	Ti-β (1.8)	Acetone	130	4/1	7	0.6	~5
7	TS-1 (1.8)	Acetone	130	4/1			
8	Ti-β (0.6)	TBA	90	1/3	29	0.82	

*TBA is Tertiary Butyl Alcohol*

*ND means None Detected*

- 5 The data in Table 1 showing how the conversion, oxygen content and acid content can be influenced by the choice of catalyst, proportions of materials used, choice of solvent and the reaction conditions.

10 The infra red spectrum of the unoxidised mixture of 70% tertiary butyl alcohol and 30% diesel in the region 500 to 4000 wave numbers is Figure 1 hereto and Figure 2 is an expanded version of the spectra in the region 1200 to 2000 wave numbers. Figures 3 and 4 are the corresponding spectra for the product of Run 3 and Figures 5 and 6 are the corresponding spectra for the product of Run 8. The spectra clearly show the presence of the carbonyl function with the significant increase in the peak at around 1709 and the new peak around 1650, the use of tertiary butyl alcohol as the solvent masks any indication of alcohol in the oxidised fuel.

15

Figure 7 is the infra red spectrum of the acetone/diesel mixture used as the feedstock in Run 1, which used an acetone solvent and Figure 8 is the spectrum of the oxidised product

of Run 1. The peak at 3500 in Figure 8 confirms the formation of hydroxyl groups during oxidation. In this instance the acetone masks any indication of the carbonyl groups in the oxidised fuel.

- 5 The spectra for Runs 2, 4, 6 and 7 showed a similar effect.

#### Comparative Example 1

- For comparative purposes, Runs 1 and 3 were repeated using no catalyst and also using titanium dioxide as a catalyst. The infra red spectra of the products showed no formation of  
10 carbonyl or hydroxyl groups.

#### EXAMPLE 2

- Since the quantities of fuel produced in Example 1 were too small for engine tests the performance of fuel containing the hydroxyl and carboxyl containing materials that would  
15 have been expected to be produced in Example 1 was simulated by the addition of various oxygenates to an Ultra Low Diesel Fuel (ULSADO) having the following properties:

	Density	825 Kg/m <sup>3</sup>
	KV <sub>20</sub> (cSt)	3.41
20	Sulphur Content	31 ppm
	T95	314°C

- The fuel was blended with the appropriate amount of oxygenate to achieve an oxygen content in the final blend of 2% by weight. A primary alcohol, secondary alcohol, tertiary  
25 alcohol and ketone were used. The fuel blends details are set out in Table 2.

**Table 2:**

<b>Test</b>	<b>Fuel</b>	<b>% wt oxygenate</b>
1	ULSADO Base	0
2	Base + Isodecanol	18.74
3	Base + Dimethyl Heptanol	18.0
4	Base + Dimethyl Octanol	19.75
5	Base + Dimethyl Heptanone	17.75

Testing was carried out in a VW Golf 1.9 Turbo-Direct Injection engine, this is a 1.9 litre turbo-charged intercooled direct injection engine with an oxidation catalyst mounted very close to the engine block, exhaust gas recirculation, and an electronically controlled distributor fuel pump with a needle lift sensor allowing for closed loop control of injection timing.

The fuel blends were tested according to a specific test protocol and involved testing a base fuel against a different test fuel each day. The base fuel was tested first followed by the test fuel which was tested three times in succession followed by a final base fuel test (base1, test1, test2, test3, base2). Each of these five tests comprised a hot ECE+EUDC drive cycle. Gaseous and particulate emissions were collected for each test.

## **Results and Discussion**

Figure 9 and Table 3 show the data for the Particulate (PM) and NO<sub>x</sub> emissions measured for each fuel. The bars show the 95% least significant difference limits and if these do not overlap then there is said to be significant difference between fuels. All 4 oxygenates showed substantial and significant reductions in particulate emissions relative to the base ULSADO fuel with an average reduction of 21.9%. There was no statistically significant difference in the amount of particulate reductions seen between the type of oxygenates

used. The 4 oxygenated blends generated somewhat greater absolute emissions of NO<sub>x</sub> than did the ULSADO with an average increase of 2.4%. However, for the tertiary alcohol and the ketone these increases were very small and not statistically significant at the 95% level.

5

Figure 10 and Table 3 show the relative change in emissions of each oxygenated blend compared with the base fuel. Reductions in particulate emissions (PM) varied from 19.8% (tertiary alcohol) to 22.6% (primary & secondary alcohols and ketone). The corresponding increases in NO<sub>x</sub> emissions relative to ULSADO were 0.5% (tertiary), 1.0% (ketone), 3.8% (primary) and 4.4% (secondary). The addition of an oxygenate to the base diesel fuel also had the effect of increasing hydrocarbon (HC) and carbon monoxide (CO) emissions, although these can be more easily controlled by the use of a typical exhaust oxidation catalyst in the engine exhaust system.

10

15 **Table 3:**

<b>Fuel</b>	<b>CO</b>	<b>CO<sub>2</sub></b>	<b>HC</b>	<b>NO<sub>x</sub></b>	<b>PM</b>
	g/km	g/km	g/km	g/km	g/km
<b>ULSADO</b>	0.230	130.1	0.064	0.479	0.047
<b>Primary</b>	0.297	128.5	0.071	0.497	0.037
<b>Secondary</b>	0.292	128.4	0.077	0.500	0.037
<b>Tertiary</b>	0.270	129.4	0.075	0.481	0.038
<b>Ketone</b>	0.280	128.2	0.081	0.484	0.037

**Difference from ULSADO base  
[%]**

<b>Fuel</b>	<b>CO</b>	<b>CO<sub>2</sub></b>	<b>HC</b>	<b>NO<sub>x</sub></b>	<b>PM</b>
<b>Primary</b>	29.27095	-1.2042	9.98703	3.827418	-22.6033
<b>Secondary</b>	27.23975	-1.28107	19.84436	4.384134	-22.6033
<b>Tertiary</b>	17.51904	-0.56367	16.73152	0.487126	-19.7889
<b>Ketone</b>	22.01668	-1.46042	26.07004	0.974252	-22.6033

**Comparative Example 2**

Example 1 of United States Patent 5 114 433 and Example 1 of United States Patent 5 114 434 were repeated at one tenth scale using the distillate fuel used in Example 1 above. Analysis of the product mixture showed no indication that the diesel fuel had  
5 been oxidised.

**CLAIMS**

1. Distillate fuel having hydroxyl and/or carbonyl groups chemically bound to paraffinic carbon atoms within the distillate fuel molecules in an amount to provide at least 0.1 wt % oxygen in the fuel.  
5
2. Distillate fuel according to Claim 1 containing at least 0.3 wt % oxygen.
3. Distillate fuel according to Claim 1 or Claim 2, in which 70% or more of the oxygen within the distillate fuel molecules is in the form of hydroxyl or carbonyl groups.  
10
4. Distillate fuel according to any of the preceding Claims, containing 0.5 to 10 wt % oxygen.
- 15 5. Distillate fuel according to any of the preceding claims in which the hydroxyl groups are secondary and/or tertiary hydroxyl groups.
6. Distillate fuel according to any of the preceding Claims, boiling in the range 150 to 400°C.  
20
7. Distillate fuel according to any of the preceding Claims, having a 95 vol % boiling point no greater than 370°C.
8. Distillate fuel according to Claim 6, having a 95 vol % boiling point no greater than 360°C.  
25

9. Distillate fuel according to any of the preceding Claims, containing less than 350 ppm sulphur.
10. Distillate fuel according to Claim 9 containing less than 50 ppm sulphur.
- 5 11. Distillate fuel according to any of the preceding Claims, containing less than 11 wt % polycyclic aromatics.
- 10 12. Distillate fuel according to any of the preceding Claims, containing no more than 15 wt % olefins.
13. Distillate fuel according to any of the preceding Claims, having a cetane number above 50.
- 15 14. Distillate fuel according to Claim 13, having a cetane number of at least 52.
15. Distillate fuel according to any of the preceding claims having a Total Acid Number of less than 1 mgKOH/gram.
- 20 16. Distillate fuel according to any of the preceding Claims, containing a cetane improver.
17. Distillate fuel according to any of the preceding Claims, containing a dispersant.
- 25 18. Distillate fuel according to any of the preceding Claims, containing a lubricity-enhancing additive.

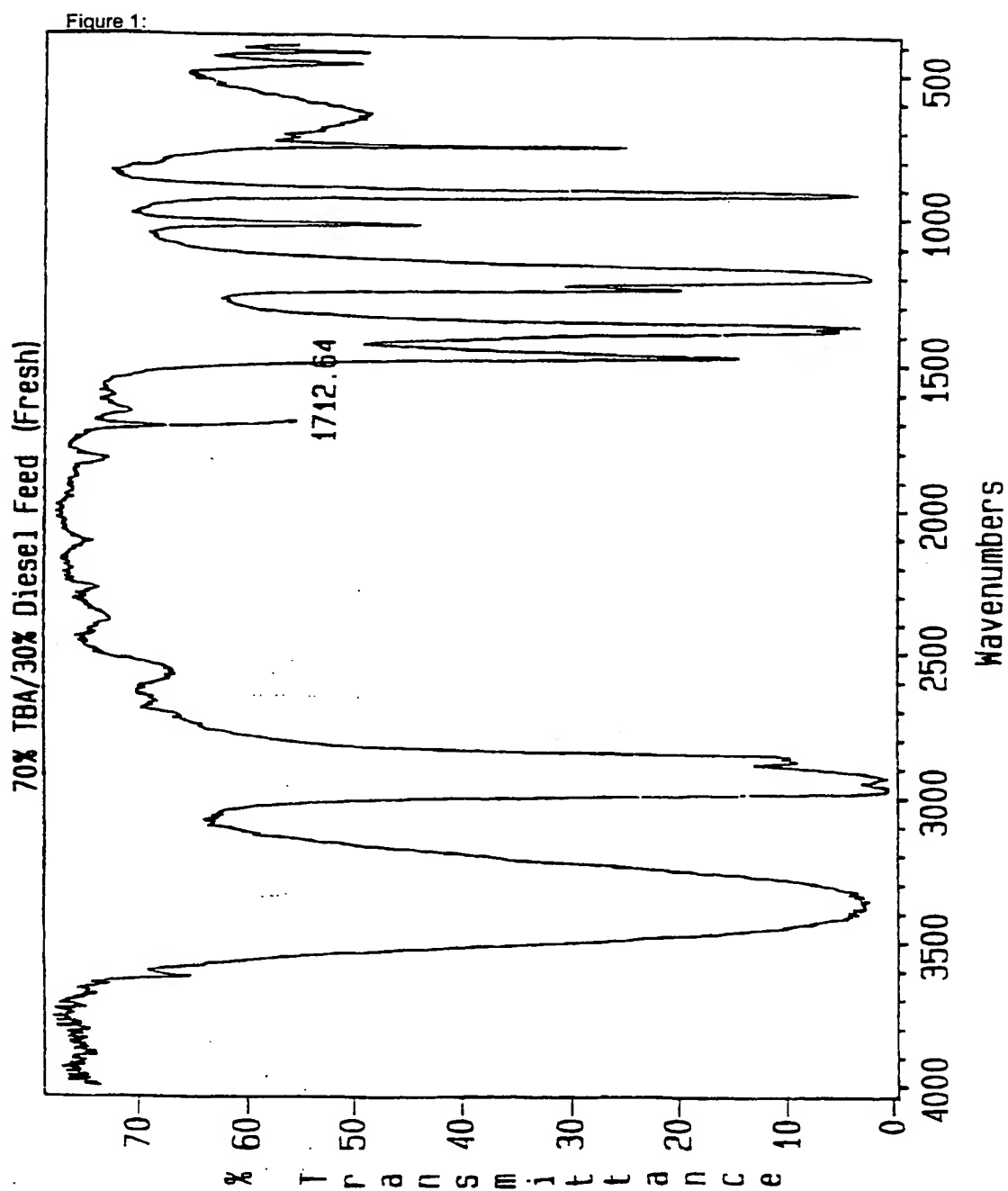
19. Distillate fuel according to any of the preceding Claims, containing a low temperature flow improver.
- 5 20. Automotive diesel fuel which is a distillate fuel according to any of the preceding Claims.
21. The reduction in the production of particulate emissions from fuel combustion in diesel engines comprising using a distillate fuel having hydroxy and/or carbonyl groups chemically bound to paraffinic carbon atoms within the distillate fuel molecules in an amount to provide at least 0.1 wt% oxygen in the fuel.
- 10
22. The reduction according to Claim 21, in which the distillate fuel contains at least 0.3 wt % oxygen.
- 15
23. The reduction according to Claim 21 or Claim 22, coupled with the use of an oxidation catalyst to reduce the hydrocarbon and carbon monoxide content of the exhaust gases from the diesel engine.
- 20 24. A process comprising selectively oxidising paraffinic carbon atoms in a distillate fuel to provide hydroxyl and/or carbonyl groups bonded to aliphatic carbon atoms in the distillate fuel and an oxygen content in the fuel of at least 0.1 wt %.
- 25 25. A process according to Claim 24, in which the fuel has an oxygen content of at least 0.3 wt %.

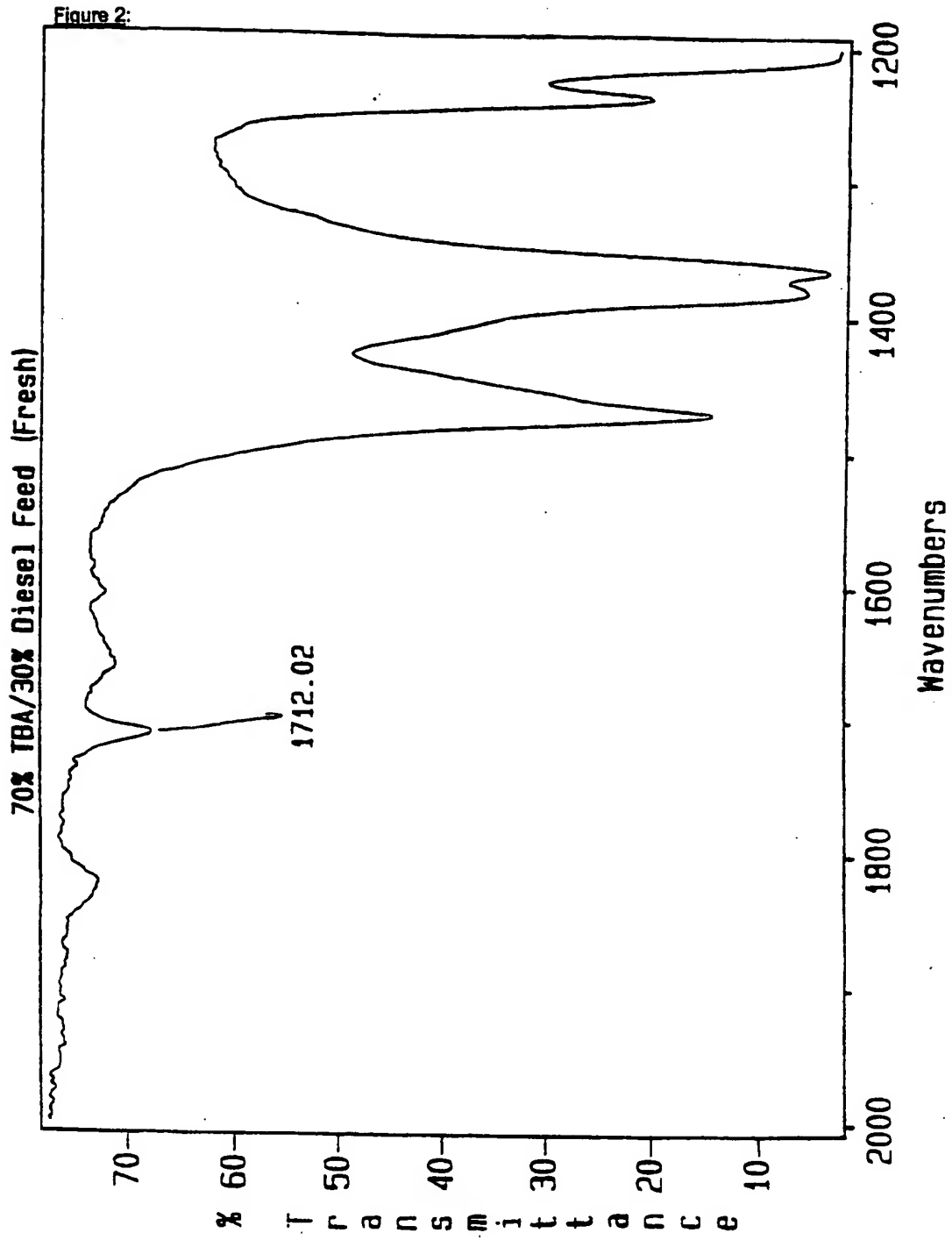


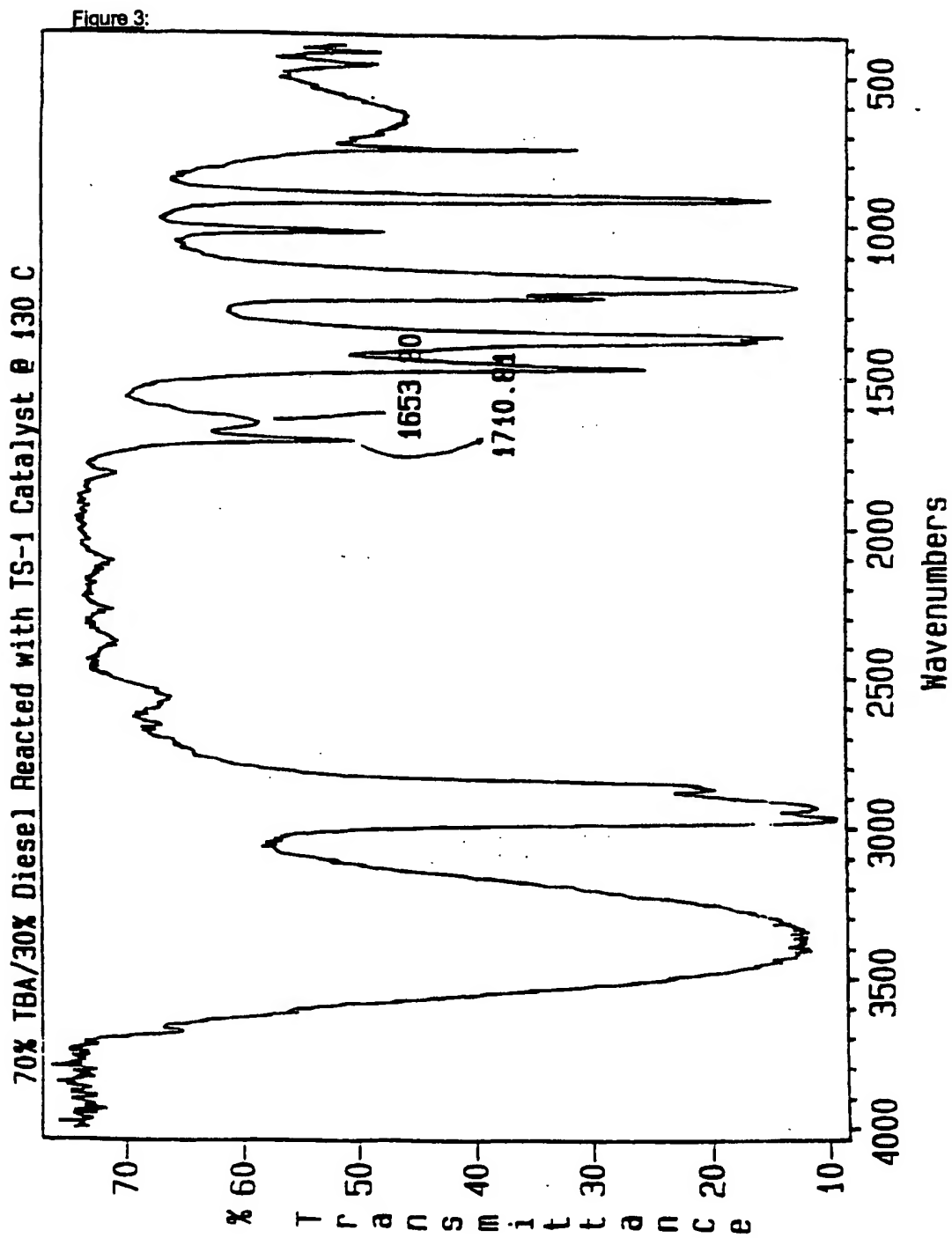
26. A process according to Claim 24 or Claim 25, in which the fuel boils in the range 150 to 400°C.
27. A process according to any of Claims 24 to 26, in which the distillate fuel has a sulphur content below 300 ppm.
28. A process according to Claim 27 in which the distillate fuel has a sulphur content below 50 ppm.
29. A process according to any of Claims 24 to 28 in which the distillate fuel has an olefin content below 15 wt%.
30. A process according to any of Claims 24 to 29 in which the fuel is oxidised by contact with an oxidising agent in the presence of a titanium and silicon containing catalyst.
31. A process according to any of Claims 24 to 30 in which the fuel is oxidised with hydrogen peroxide.
32. A process according to Claim 31, in which the fuel is oxidised by contact with hydrogen peroxide in the presence of a titanium silicalite catalyst at a temperature between 50 and 150°C.
33. A process according to Claim 31 or Claim 32, in which the hydrogen peroxide is produced in situ.

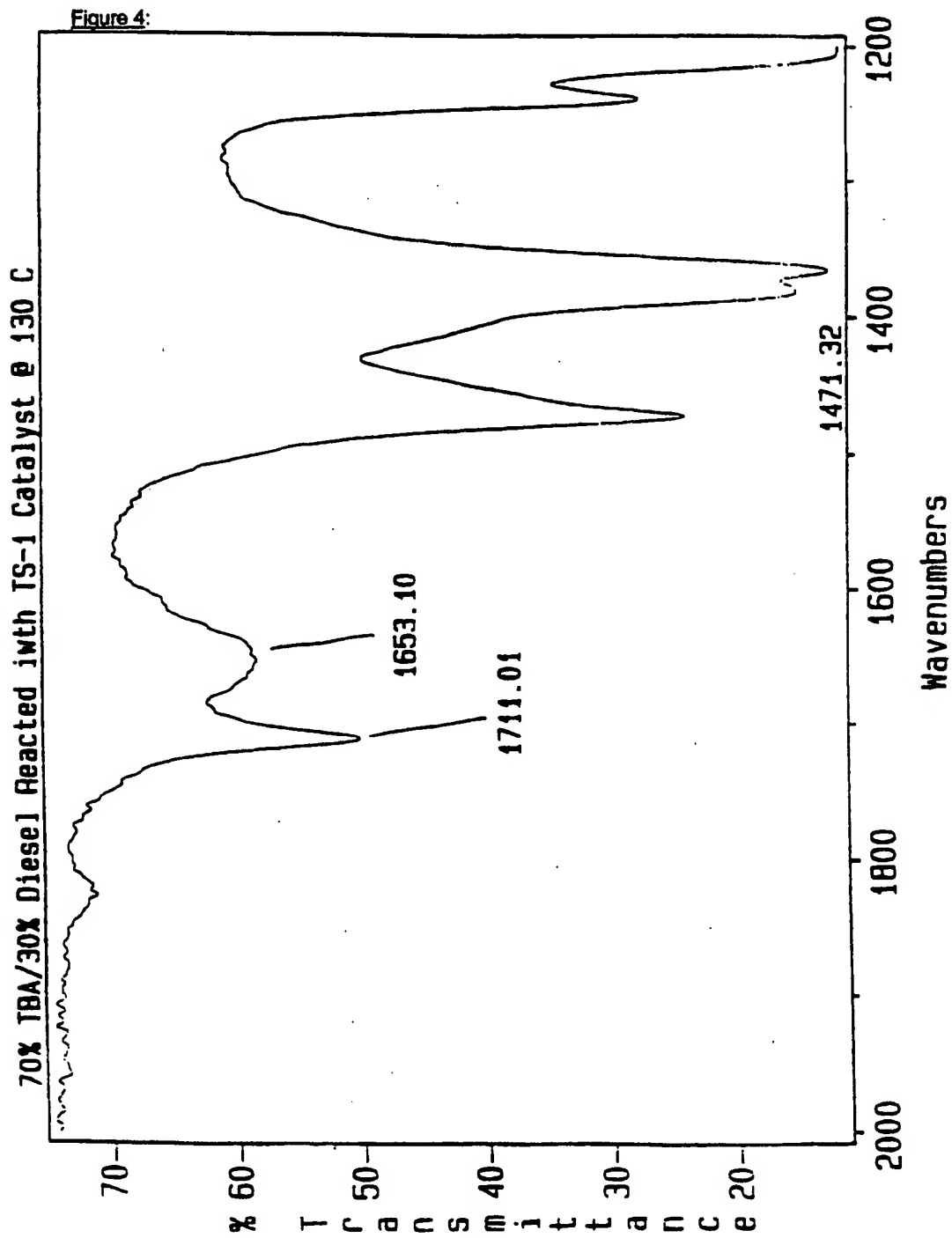
34. A process according to Claim 33 in which a dual catalyst system is used to both produce the hydrogen peroxide and catalyse the oxidation of the fuel.
- 5 35. A process according to any of the preceding Claims 24 to 34, in which the selective oxidation takes place in a reactor downstream of a refinery hydrofiner.
36. A process according to any of Claims 24 to 35, in which oxidized sulphur and/or nitrogen species are removed from the oxidized fuel.
- 10 37. A process according to Claim 36, in which the removal is by washing.
38. A process according to Claim 36, in which the removal is by distillation.
39. A process according to Claim 36, in which the removal is by adsorption.

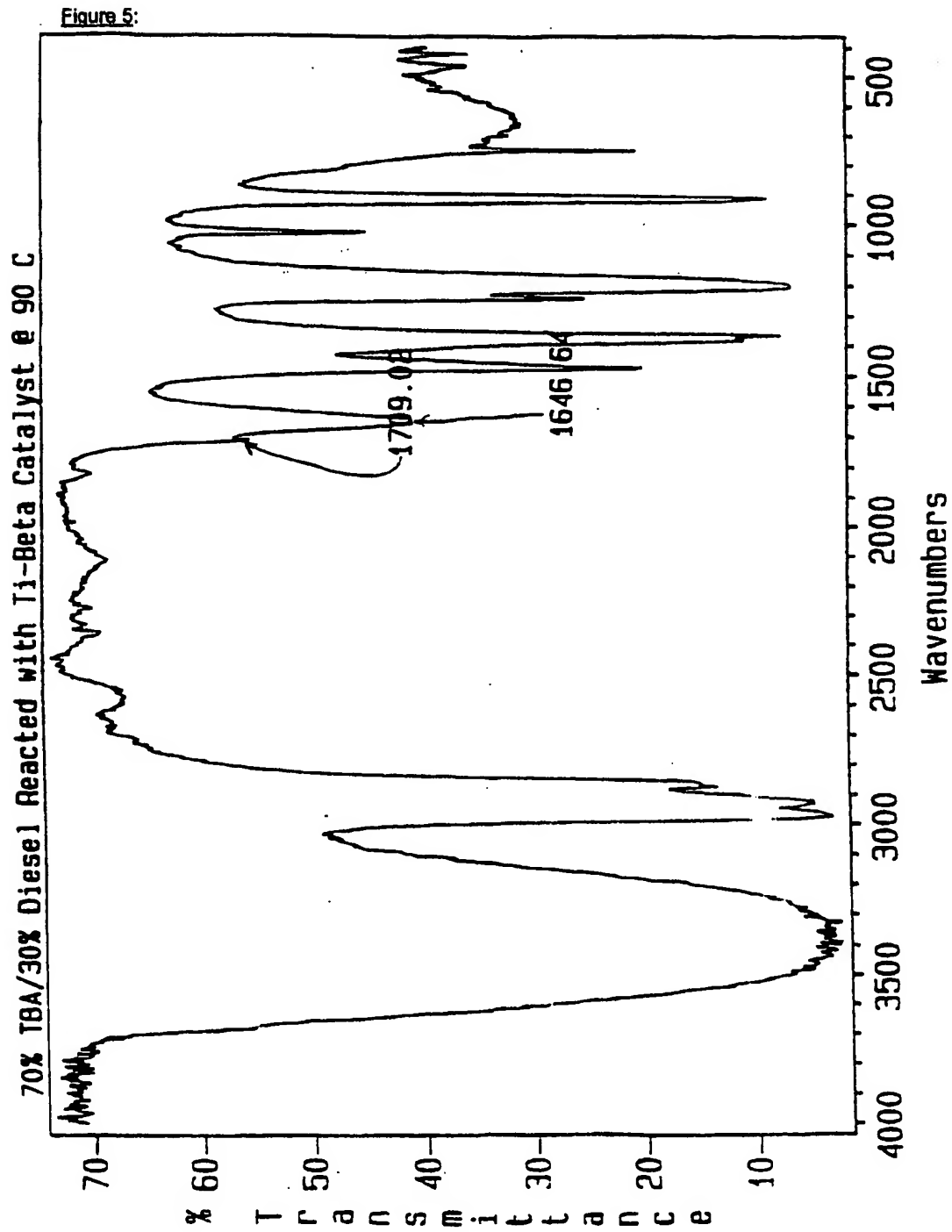
15

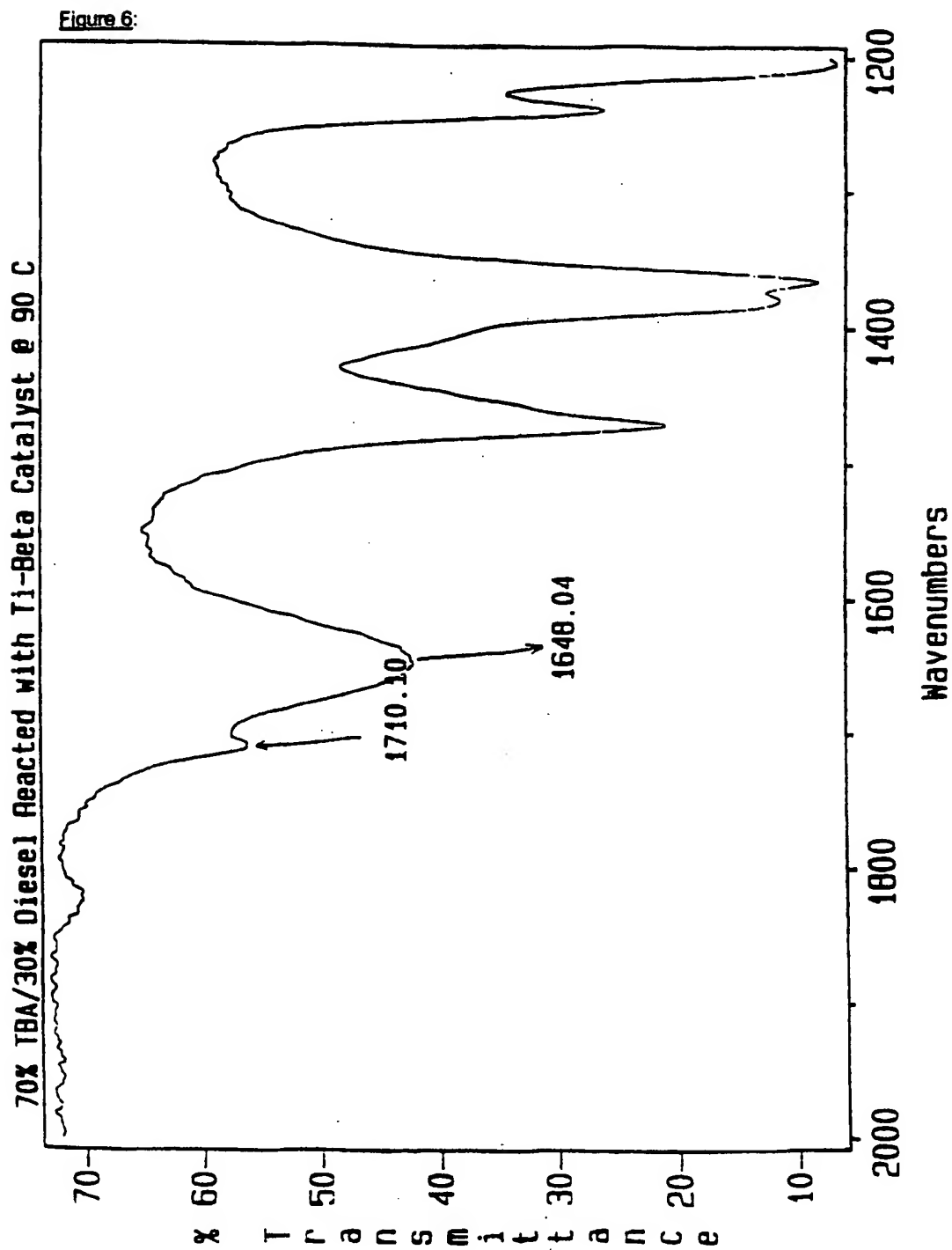














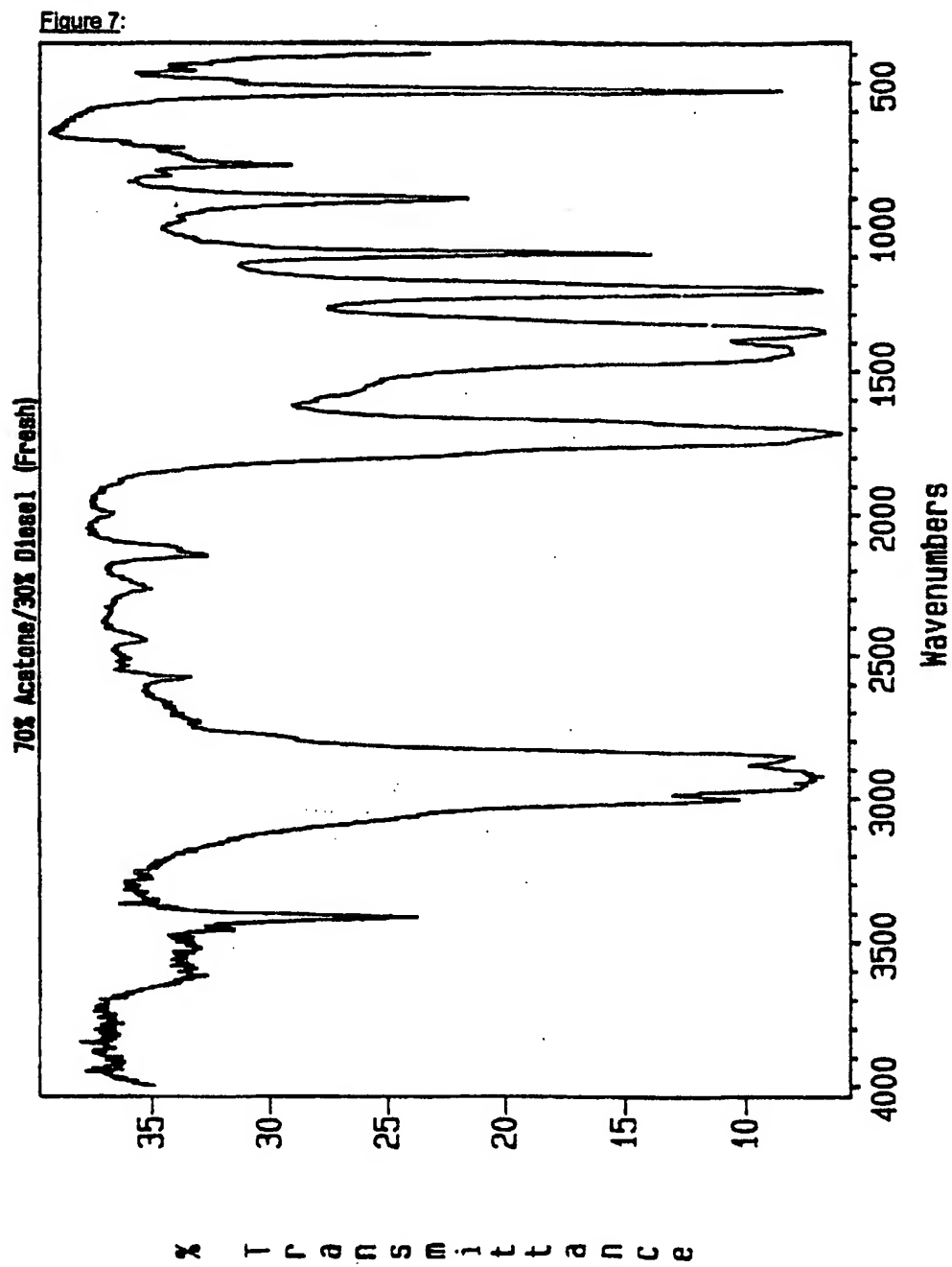
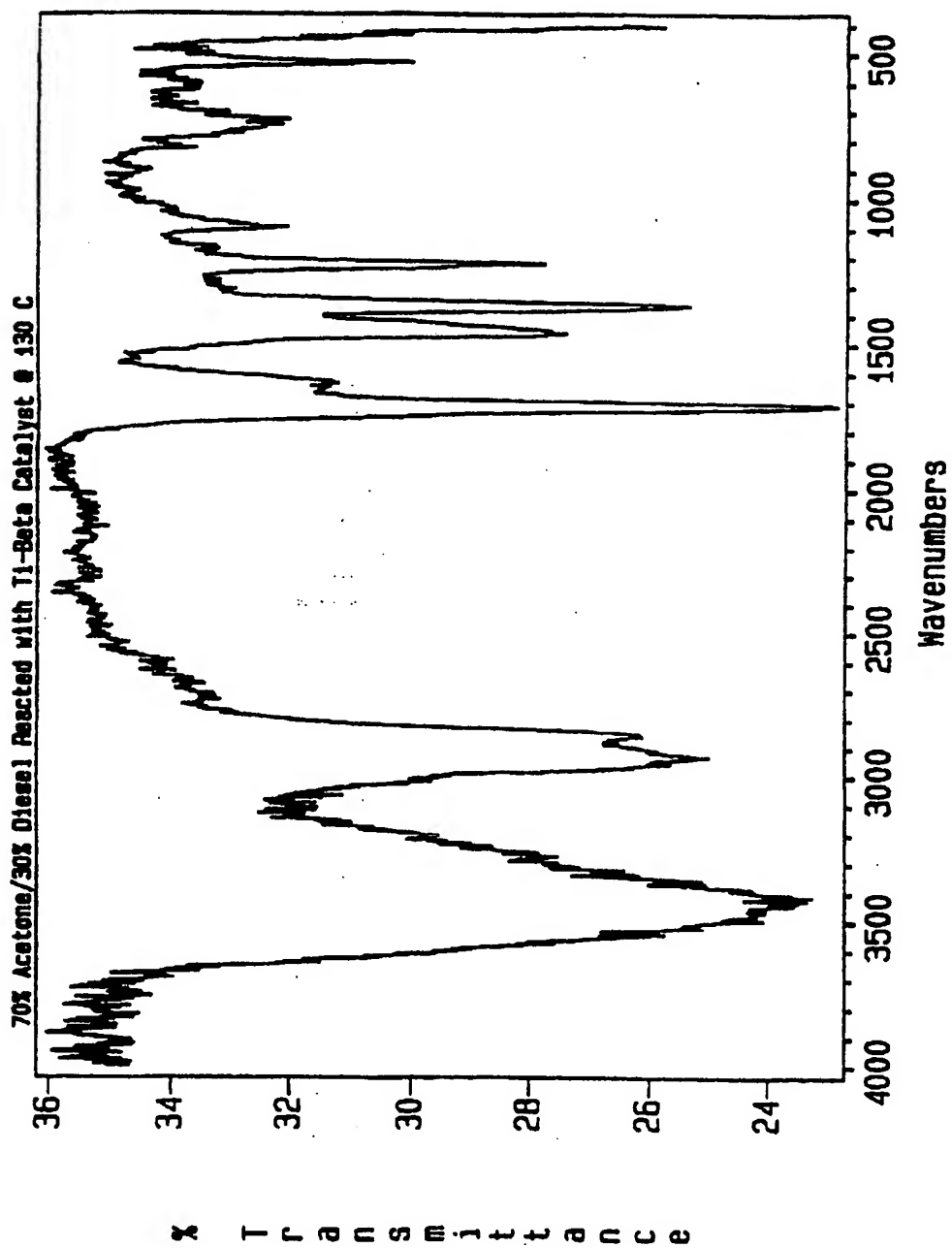


Figure 8:



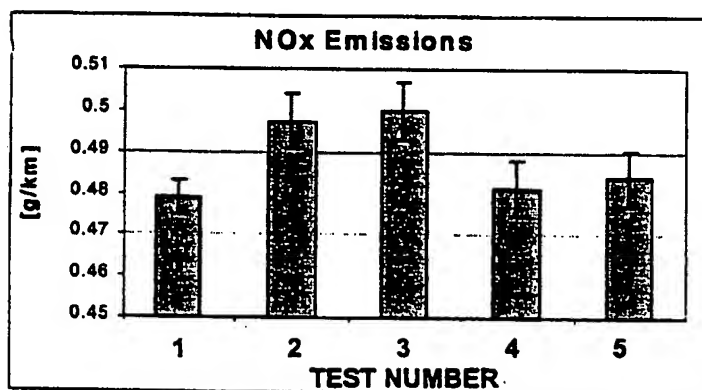
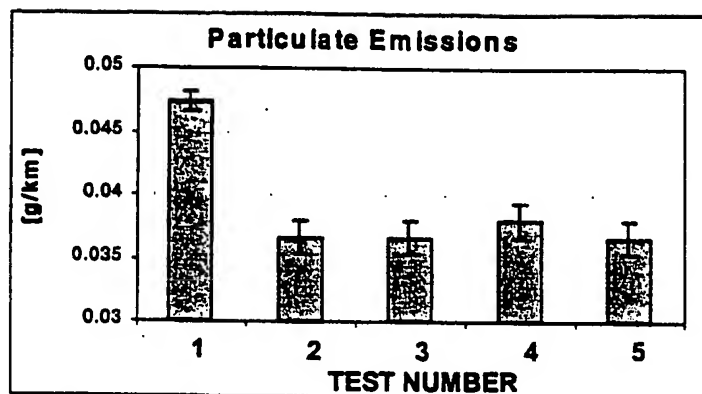
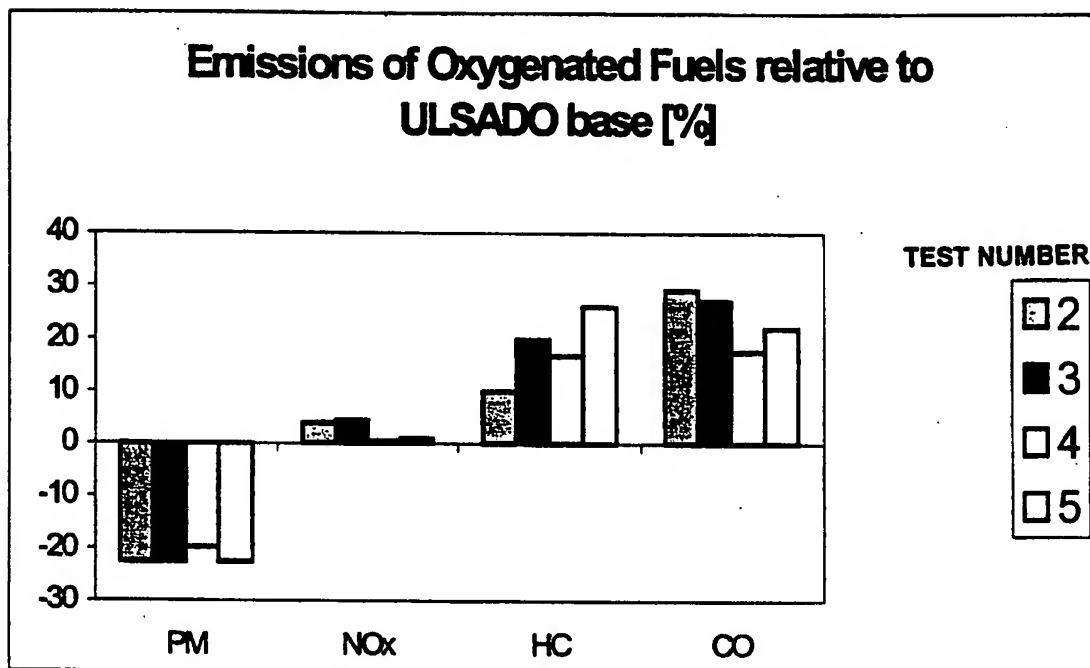
**Figure 9:**

Figure 10:



# INTERNATIONAL SEARCH REPORT

Int. Appl. No.  
PCT/EP 00/10829

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10L1/02 C10G27/12 C10G67/12 C10L1/18 C10L10/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10L C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 05740 A (EXXON RESEARCH ENGINEERING CO) 12 February 1998 (1998-02-12)  the whole document	1-4, 6-14, 20-22
X	US 4 378 973 A (SWEENEY WILLIAM M) 5 April 1983 (1983-04-05) the whole document	1-4, 6-8, 20-22
X	US 5 645 613 A (YAKOBSON DENNIS L ET AL) 8 July 1997 (1997-07-08)  the whole document	1-4, 6-11, 13, 14, 21, 22
X	WO 99 21943 A (SUPPES GALEN J ; UNIV KANSAS CENTER FOR RESEARC (US)) 6 May 1999 (1999-05-06) the whole document	1-4, 9-12, 16, 19-22
-/-		



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*A\* document member of the same patent family

Date of the actual completion of the international search

27 March 2001

Date of mailing of the international search report

03/04/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentkan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

De La Morinerie, B

**Int**      **ional Application No**

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ional Application No

PCT/EP 00/10829

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9805740 A	12-02-1998	US 5807413 A	15-09-1998
		AU 717092 B	16-03-2000
		AU 3600297 A	25-02-1998
		BR 9710862 A	17-08-1999
		CA 2259206 A	12-02-1998
		CN 1225666 A	11-08-1999
		EP 0948585 A	13-10-1999
		JP 2000515575 T	21-11-2000
		NO 990486 A	02-02-1999
		TW 411363 B	11-11-2000
US 4378973 A	05-04-1983	NONE	
US 5645613 A	08-07-1997	US 5324335 A	28-06-1994
		US 5543437 A	06-08-1996
		US 5621155 A	15-04-1997
		US 5620670 A	15-04-1997
		US 5763716 A	09-06-1998
		AU 6028894 A	15-08-1995
		WO 9520558 A	03-08-1995
		US 5504118 A	02-04-1996
		US 5506272 A	09-04-1996
		US 5500449 A	19-03-1996
WO 9921943 A	06-05-1999	AU 1280299 A	17-05-1999
		EP 1027409 A	16-08-2000
		US 6056793 A	02-05-2000
US 5324335 A	28-06-1994	WO 9520558 A	03-08-1995
		AU 6028894 A	15-08-1995
		US 5504118 A	02-04-1996
		US 5645613 A	08-07-1997
		US 5621155 A	15-04-1997
		US 5506272 A	09-04-1996
		US 5543437 A	06-08-1996
		US 5500449 A	19-03-1996
		US 5620670 A	15-04-1997
		US 5763716 A	09-06-1998
		AU 697448 B	08-10-1998
WO 9834998 A	13-08-1998	US 5814109 A	29-09-1998
		BR 9807171 A	25-01-2000
		EP 0958334 A	24-11-1999
		NO 993739 A	07-10-1999
		ZA 9800621 A	22-07-1998
US 4632675 A	30-12-1986	US 4702748 A	27-10-1987
EP 0905217 A	31-03-1999	JP 11106763 A	20-04-1999
EP 0376453 A	04-07-1990	AT 96140 T	15-11-1993
		AU 628439 B	17-09-1992
		AU 4636289 A	28-05-1990
		CA 2002494 A	08-05-1990
		DE 68910101 D	25-11-1993
		DE 68910101 T	30-06-1994
		DK 163890 A	23-08-1990
		ES 2059782 T	16-11-1994

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/EP 00/10829

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0376453 A		WO 9005126 A	17-05-1990
		JP 3049086 B	05-06-2000
		JP 3503741 T	22-08-1991
		KR 151712 B	15-10-1998
		NO 173821 C	09-02-1994
		RU 2036191 C	27-05-1995
		US 5021607 A	04-06-1991
EP 0115382 A	08-08-1984	AU 2416684 A	02-08-1984
		CA 1202927 A	08-04-1986
		WO 8402716 A	19-07-1984
		JP 60500450 T	04-04-1985
		NO 843369 A	23-08-1984
		ZA 8400126 A	28-08-1985